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TITLE: FUEL GAS FEED METHOD FOR FUEL CELL
GENERATING SYSTEM

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ABSTRACT:

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PURPOSE: To make a load temperature rise from low temperature performable as well as to aim at the shortening of starting time for a cell, by housing each adsorbent of moisture and carbon monoxide stratifyingly in a feed manifold of the fuel gas made up of reforming methanol into hydrogen rich gas with a reformer.

CONSTITUTION: A moisture adsorbent 8 and a carbon monoxide adsorbent 9 are stratifyingly housed in a manifold 3 at the fuel gas inlet side of a cell 2.

With this, a temperature rise by cell reaction heat from a low state (about 40°C) in cell temperature comes possible without entailing any poisoning due to carbon monoxide out of a fuel electrode catalyzer and an increment due to moisture of a phosphate electrolyte so that rise time of the cell 2 is sharply reducible, and when the cell 2 becomes more than the specified temperature, the adsorbing moisture and the adsorbing carbon monoxide are separated, thus these adsorbents 8 and 9 are regenerable.

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⑮ 発明の名称 燃料電池発電システムの燃料ガス供給方式

⑯ 特 願 昭62-63481

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明 細 書

1. 発明の名称

燃料電池発電システムの燃料ガス供給方式

2. 特許請求の範囲

① メタノールをリフオーマで改質した燃料ガスを電池に供給する入口側マニホールド内に、水分及び一酸化炭素の各吸着剤を層状に収納し、電池の低温起動時前記各吸着剤により前記燃料ガス中の水分及び一酸化炭素を夫々吸着し、電池の所定温度以上で前記吸着水分及び吸着一酸化炭素を離脱させて前記各吸着剤を再生せしめることを特徴とする燃料電池発電システムの燃料ガス供給方式。

3. 発明の詳細な説明

(イ) 産業上の利用分野

本発明はメタノールリフオーマを用いたりん酸燃料電池発電システム、特に可搬用に適する小型発電システムの燃料ガス供給方式に関するものである。

(ロ) 従来の技術

一般に燃料電池の燃料極に供給される燃料ガスは、炭化水素燃料を燃料処理装置で改質した水素リッチガスを用いるが、原燃料として天然ガスを用いる場合、リフオーマで改質したガス中には多量(約4%)のCOを含んでおり、これが電極触媒の白金を被覆するため、このCOをシフトコンバータでCO₂に転化してCO含量を約0.5%迄低減する必要がある。そのため燃料処理装置が大型化して小型発電システムには適しない。

これに対し原燃料にメタノールを用いる場合、これを改質して得られる水素リッチガス中のCO含量は0.5%程度であるから、シフトコンバータを通すことなく、燃料ガスとして用いることができ、燃料処理装置が簡素化されて小型発電システムに適している。

一方COによる白金触媒の被覆は、電池温度が低い程著しく、従って従来は始動時電池温度を約125℃程度に昇温して後各反応ガスを供給し、電池反応熱により電池の規定作動温度(約180～190℃)まで昇温(負荷昇温)する方法が採用されて

いた。しかしこの方法では電池の立上り時間が長くなるという問題があった。

又燃料ガス中には多量(約10%)の水分を含んでおり、通常減湿器で水分を除去して後電池に供給する方法がとられているが、これ又装置を複雑化することになる。

もし水分を除去することなしに低温(約40℃)から負荷昇温を開始すれば、電池温度が約40℃から約100℃に達するまでの間、供給燃料ガス(温度約160℃)が電池で冷却される。そのため燃料ガス中のスチームが水となり、これがマトリックス中のりん酸電解液に吸収されて液量が増大するという問題があった。

(ハ) 発明が解決しようとする問題点

この発明は低温(約40℃)からの負荷昇温を可能として電池の起動時間を短縮し、しかも改質ガス中のCOによる触媒被毒及び改質ガス中の水分によるりん酸電解液増量の問題を解消して電池特性及び寿命に支障をきすことがないようにしたものである。

本発明燃料電池発電システムの実施例を図について説明する。

メタノールリフオーマ(1)は周知のようにメタノールと水の混合液を気化したガスが改質触媒層を通る間に燃料ガスに改質される。尚出力5kwの燃料電池に対応する小型リフオーマの立上り時間は約5～8分間である。

電池(2)は燃料ガスの入口及び出口各マニホルド(3)(3')と反応空気の入口及び出口各マニホルド(4)(4')[第1図の場合]もしくは空気(反応空気と冷却空気)の入口及び出口各マニホルド(40)(40')[第2図の場合]とを有し、更に第1図の場合は冷却ガスの入口及び出口各マニホルド(5)(5')を有する。

電池(2)の始動に際し、第1図実施例のようにブロワ(BW)でリフオーマ(1)の運送ガス(6)をマニホルド(5)を経て冷却ガス通路に送り込むか、又は第2図実施例のようにバーナー(7)で加熱された空気をマニホルド(40)を経て電池に送り込み、電池温度を約5～8分で40℃に昇温す

(ニ) 問題点を解決するための手段

この発明はメタノールをリフオーマで水素リッチガスに改質した燃料ガスを電池燃料極に供給する入口側マニホルド内に、水分及び一酸化炭素の各吸着剤を層状に収納し、電池の低温起動時燃料ガス中の前記水分及び一酸化炭素を夫々吸着除去し、ついで電池の所定温度以上で前記吸着水分及び前記吸着一酸化炭素を離脱せしめて両吸着剤を再生させるものである。

(ホ) 作用

この発明では燃料ガスの入口側マニホルド内に水分及び一酸化炭素の各吸着剤が収納されているため、燃料極触媒の一酸化炭素による被毒やりん酸電解液の水分による増量を起すことなく電池温度が低い段階(約40℃)から電池反応熱による昇温が可能となって電池の立上り時間を著しく短縮できる。また電池が所定温度以上になると吸着水分及び吸着一酸化炭素が離脱して各吸着剤を再生することができる。

(ヘ) 実施例

る。

改質燃料ガス中には約0.5～0.3%の一酸化炭素(CO)と約10%の水分(スチーム)が含まれている。

本発明では電池(2)の燃料ガス入口側マニホルド(3)内に、第3図に示すよう水分吸着剤(8)と一酸化炭素吸着剤(9)が層状に収納されている。

水分吸着剤(8)は例えばシリカゲルや活性アルミナを径約2～3mm、長さ約8mmのペレット状とした成型体を隙間ができるようステンレス製金網(10)で包み、ガス入口側に配置されている。

一酸化炭素吸着剤(9)は、白金黒もしくはパラジウム黒を担持したカーボンペーパーやモリブデンを添加したアルミナ(Mo/AI₂O₃)などであり、一例として白金触媒を担持した燃料電池のガス極を用い、これを巾約5mm～10mmに裁断して前記と同様ステンレス製金網(10)で包み、水分吸着剤(8)に隣接配置される。尚マニホルド(3)内は、スタック積重方向のステンレス製ガイド板(11)により区分してもよい。

このような燃料ガス入口側マニホルド(3)を電池(2)に取付けたとき電池スタック面とステンレス製金網(10)との間に拡散間隔(12)が形成される。

次に本発明発電システムの作動を説明する。

電池始動に際し前記の如く電池温度を約40℃に昇温して後、各反応ガスを供給して電池反応熱により昇温を開始する。このときリフォーマ(1)で生成した燃料ガスは入口マニホルド(3)を経て電池(2)の燃料極に供給されるが、供給初期マニホルド(3)内の各吸着剤(8)(9)の温度が低いので、燃料ガス中のスチームは水として吸着剤(8)に吸着し、ついで燃料ガス中の一酸化炭素は吸着剤(9)に吸着し、水分及び一酸化炭素の大部分が除かれた燃料ガスが電池(2)に送られる。

電池温度は反応熱により短時間で約100℃以上に昇温しているので、その後燃料ガス中の水分(スチーム)は、電池電解液に吸収されることなく又一酸化炭素は燃料極の触媒を殆ど被覆することなく、規定作動温度(約180~200℃)に達して定格

運転に入る。

この定格運転に入ると、吸着剤(8)に吸着されている水分はスチームとして離脱すると共に吸着剤(9)に吸着されている一酸化炭素も離脱し、両吸着剤(8)(9)が再生されて次の始動に備えることができる。

(ト) 発明の効果

本発明によれば燃料ガスの入口マニホルド内に、水分及び一酸化炭素の各吸着剤が収納されてリフォーマで生成した燃料ガス中の水分及び一酸化炭素を夫々吸着するので、電池温度が低い段階(約40℃)から反応熱による昇温を開始してもりん酸電解液の水分による増益や燃料極触媒の被覆を起すことがなく、低温から効率のよい反応熱による昇温が可能となって電池の立ち上がり時間を著しく短縮できる。又電池が所定温度以上になると吸着水分及び吸着一酸化炭素が離脱して各吸着剤を再生することができるなどの利点を有し、発電システムの構成も従来方式に比しコンパクト化され特に小容量の燃料電池に好適するものである。

4. 図面の簡単な説明

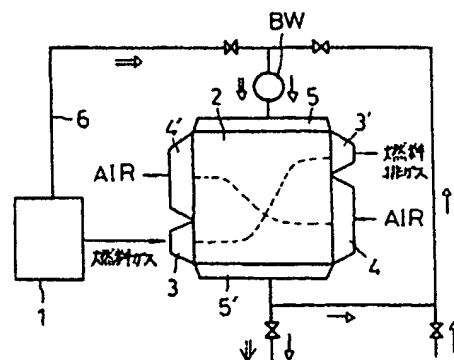
第1図は本発明による燃料電池発電システムのブロック図、第2図は同上の他実施例を示すブロック図、第3図は本発明による燃料ガス入口マニホルドを示し、(イ)は縦断側面図、(ロ)は縦断正面図、(ハ)は横断平面図である。

1: リフォーマ、2: 電池、3: 燃料ガス入口マニホルド、6: リフォーマ製造ガス、7: パーナー、8: 水分吸着剤、9: 一酸化炭素吸着剤、10: ステンレス金網。

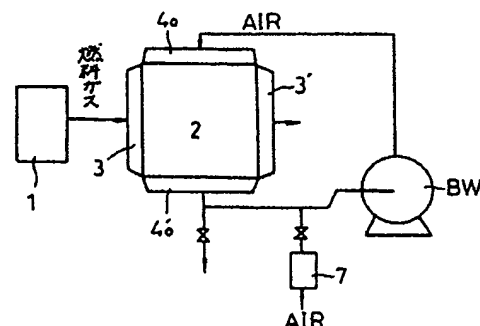
出願人 三洋電機株式会社

代理人 弁理士 西野卓嗣(外1名)

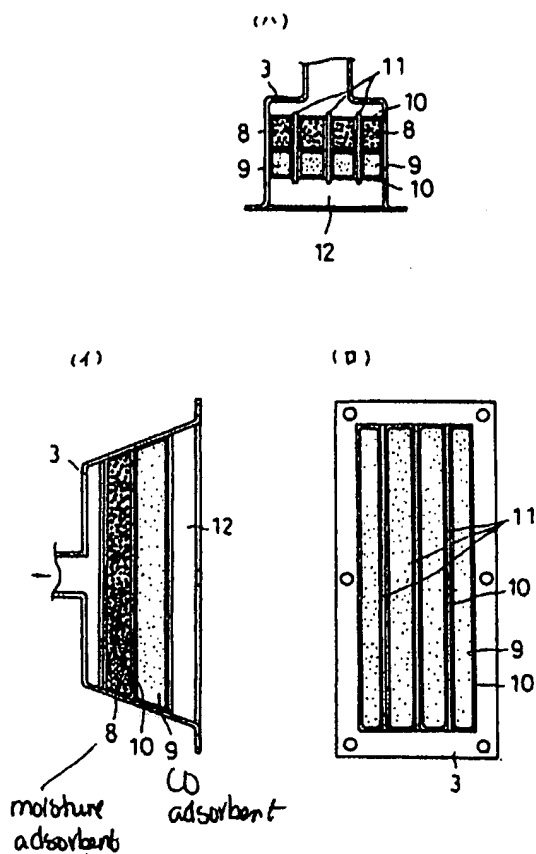
第1図



第2図



第3圖



(12) Patent Gazette (A) (19) Japan Patent and Trademark Office (JP) (11) Kokai Patent Application No. S63-228572
(43) Laid Open: September 22, 1988

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| (21) Application No. | S62-63481 | |
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Specification

1. Title

Fuel gas delivery system for fuel cell generating system

2. Claims

① A fuel gas delivery system for fuel cell generating system which is characterized by housing various adsorbents for moisture and carbon monoxide in stratified form in an intake manifold, which delivers fuel gas, which is methanol reformed by a reformer, to a cell, so that the moisture and carbon monoxide in the aforementioned fuel gas are respectively adsorbed by the various aforementioned adsorbents when the cell is cold-started, and the aforementioned adsorbed moisture and carbon monoxide are released at above a specified temperature in the cell, thereby regenerating both adsorbents.

3. Detailed Description

(a) Field of Industrial Application

This invention pertains to phosphoric acid fuel cell generating systems that use a methanol reformer, and specifically pertains to the fuel gas delivery system for small-scale electrical generating systems suitable for portability.

(b) Prior Art

Hydrogen-rich gas produced by reforming hydrocarbon fuel with fuel processing equipment is generally used as the fuel gas that is delivered to the fuel electrode in a fuel cell, but when natural gas is used as the raw fuel, the reformed gas from the reformer contains large quantities (approximately 4%) of CO, and since this will contaminate the platinum in the electrode catalyst, it is necessary to decrease the CO content to approximately 0.5% by using a shift converter to convert this CO to CO₂. Consequently, fuel-processing equipment has become large and unsuitable for small-scale generation systems.

In contrast, since the CO content in the hydrogen-rich reformed gas is only about 0.5% when methanol is used as the raw fuel, it can be used as fuel gas without passing it through a shift converter, simplifying the fuel processing equipment and making it more suited to small-scale generation systems.

Meanwhile, the lower the cell temperature, the more pronounced the CO-contamination of the platinum catalyst, and consequently, methods have been used in the past in which, when starting the cell, various reaction gases were supplied after heating the cell temperature to approximately 125°C, and the cell was then heated to its rated operating temperature (approximately 180–190°C) by the cell reaction heat. However, this method had problems with prolonged cell start-up times.

Fuel gases also contain large quantities (approximately 10%) of moisture, and methods also have been used in which the fuel is delivered to the cell after removing the moisture with a common condenser, but this tended to complicate the equipment.

If load heating is started from a low temperature (approximately 40°C) without removing the moisture, the delivered fuel gas (temperature of approximately 160°C) would be cooled in the cell by the time the cell temperature rose from approximately 40°C to approximately 100°C. This consequently was a problem in that steam in the fuel gas would become water, which would be adsorbed by the phosphoric acid electrolyte in the matrix, causing the fluid volume to expand.

(c) Problems to be Solved

This invention is constituted to make load heating from low temperatures (approximately 40°C) possible to shorten the cell starting time, and moreover to resolve the problems of catalyst contamination by CO in the reformed gas and phosphoric acid electrolyte expansion by moisture in the reformed gas, thereby removing hindrances to cell performance and longevity.

(d) Means of Solving Problems

This invention houses various adsorbents for moisture and carbon monoxide in stratified form in an intake manifold, which delivers fuel gas, which is methanol reformed by a reformer, to cell fuel electrodes, so that the moisture and carbon monoxide in the fuel gas are respectively adsorbed by the various aforementioned adsorbents

when the cell is cold-started, and the aforementioned adsorbed moisture and carbon monoxide are released at above a specified temperature in the cell, thereby regenerating both adsorbents.

(e) Action

By housing various adsorbents for moisture and carbon monoxide in the fuel gas intake manifold, this invention makes it possible to increase the cell temperature from a level (approximately 40°C) by means of cell reaction heat, without contaminating the fuel electrode catalyst with carbon monoxide and without causing the volume of phosphoric acid electrolyte to increase due to moisture, markedly shortening the cell start-up time. In addition, the various adsorbents can also be regenerated by the adsorbed moisture and the adsorbed carbon monoxide being released when the cell heats to above a specified temperature.

(f) Example Embodiments

Example embodiments of the fuel cell generating system of this invention will be described using the attached figures.

A methanol reformer (1) reforms natural gas as the gas, which, as is commonly known, is a vaporized mixture of liquid methanol and water, passes through a reforming catalyst layer. Further, the start-up time of a small-scale reformer compatible with a 5 kw-output fuel cell is approximately 5 to 6 minutes.

A cell (2) possesses respective fuel gas intake and exhaust manifolds (3)(3') and respective reaction air intake and exhaust manifolds (4)(4') [in the case in Figure 1] or respective air (reaction air and cooling air) intake and exhaust manifolds (4a)(4a') [in the case in Figure 2], and further, in the case in Figure 1, possesses respective cooling gas intake and exhaust manifolds (5)(5').

When the cell (2) is started, gas flue gas (6) in the reformer is forced by a blower (BW) into the cooling gas duct via the manifold (5), as shown in the example in Figure 1, or air that has been heated by a burner (7) is forced into the cell via the manifold (4), as in the example in Figure 2, raising the cell temperature to 40°C in approximately 5–6 minutes.

The reformed fuel gas contains approximately 0.5–0.3% carbon monoxide (CO) and approximately 10% moisture (steam).

In this invention, a moisture adsorbent (8) and a carbon monoxide adsorbent (9) are housed in stratified form inside the fuel gas intake manifold of the cell (2), as shown in Figure 3.

The moisture adsorbent (8) is, e.g., 2–3 mm-diameter × approximately 5 mm-long silica gel or activated alumina molded pellets that are encased in a stainless steel mesh so that spaces are formed between them, which is then disposed in the gas intake.

The carbon monoxide adsorbent (9) is alumina ($\text{Mo}/\text{Al}_2\text{O}_3$), or the like, to which carbon paper or molybdenum has been added, suspended in platinum black or palladium black, and as an example, a fuel cell gas

electrode is used in which a platinum catalyst is suspended, which is cut to approximately 5 mm–10 mm-wide and encased in stainless steel mesh (10) similar to that described above, and then disposed adjacent to the moisture adsorbent (8). Further, the inside of the manifold (3) may be subdivided in the stacking direction with stainless steel guide plates (11).

When this kind of fuel gas intake manifold is attached to a cell (2), a diffusion gap (12) is formed between the cell stack surface and the stainless steel mesh (10).

Next, the operation of the generating system of this invention will be explained.

When starting the cell, once the cell temperature has been raised to approximately 40°C, as described above, the various reaction gases are delivered and heating by cell reaction heat begins. At this time, the fuel gas produced by the reformer (1) is delivered to the fuel electrode of the cell (2) via the intake manifold (3), but since the temperature of the various adsorbents (8)(9) inside the manifold (3) is low when delivery is first started, the steam in the fuel gas is adsorbed as water by adsorbent (8) and the carbon monoxide in the fuel gas is adsorbed by adsorbent (9), so that the fuel gas is sent to the cell (2) with large portions of the moisture and carbon monoxide removed.

Since the cell temperature is raised in a short time by the reaction heat to approximately 100°C or more, it reaches its rated operating temperature (approximately 180–200°C) and begins regular operation, without moisture (steam) in the fuel gas being absorbed by the cell electrolyte and without virtually any carbon monoxide contamination of the fuel electrode catalyst.

As it begins regular operation, the moisture adsorbed by the adsorbent (8) is released as steam and the carbon monoxide adsorbed by the adsorbent (9) is released, regenerating both the adsorbents (8)(9) and preparing them for the next start.

(g) Effect

Since, according to this invention, various adsorbents for moisture and carbon monoxide are housed inside the fuel gas intake manifold to respectively adsorb moisture and carbon monoxide in the fuel gas produced by a reformer, it becomes possible to raise the cell temperature efficiently with reaction heat from a low temperature without increasing the volume of phosphoric acid electrolyte with moisture and without contaminating the fuel electrode catalyst with carbon monoxide, even when beginning to raise the cell temperature with reaction heat from a low level (approximately 40°C), thereby markedly shortening the cell start-up time. This also has the advantage of being able to regenerate the various adsorbents by releasing the adsorbed moisture and the adsorbed carbon monoxide when the cell heats above a specified temperature, making the generating system structure more compact than past systems and well suited to small-scale fuel cells.

Fig. 1

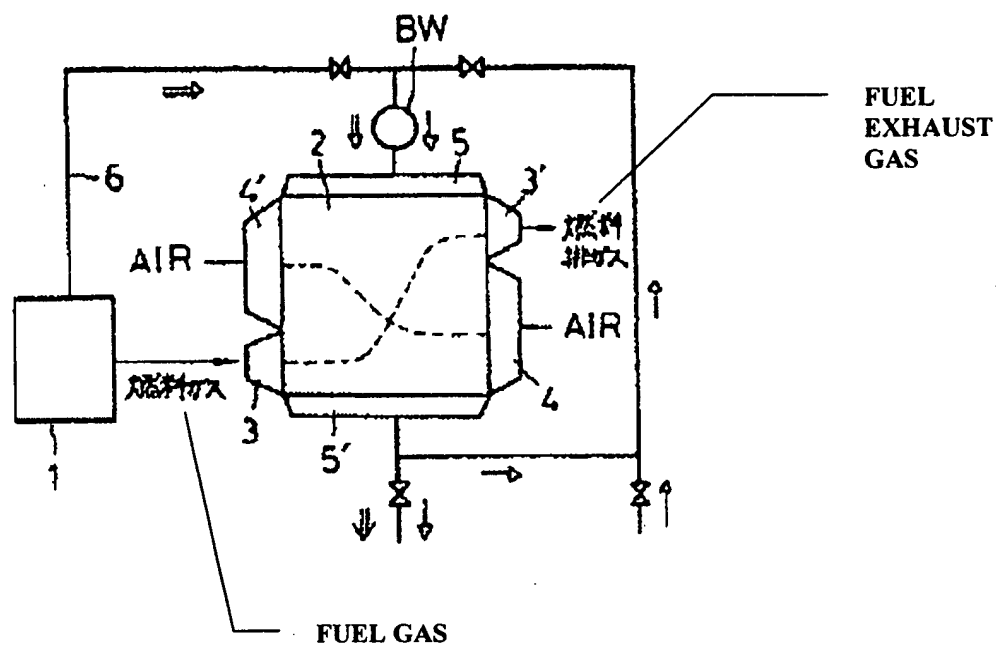



Fig. 2  **FUEL GAS**

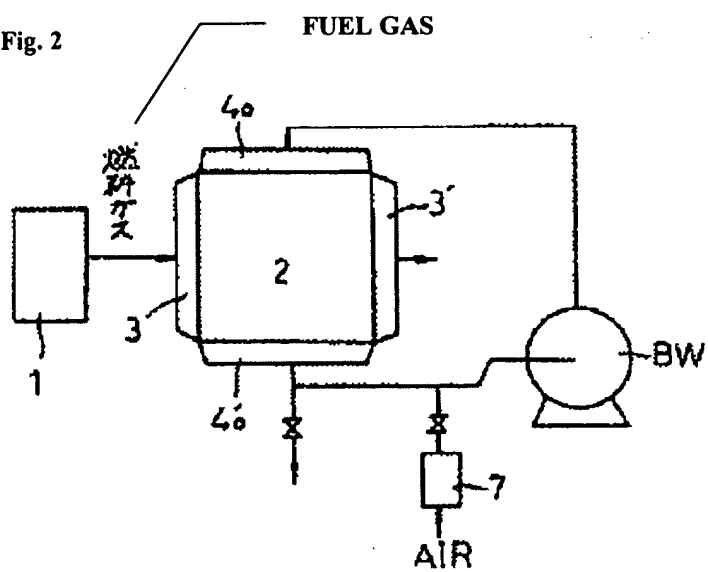
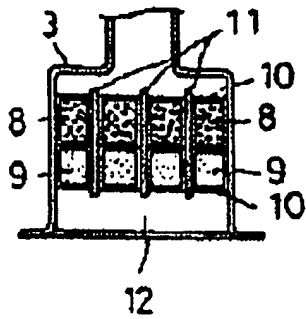
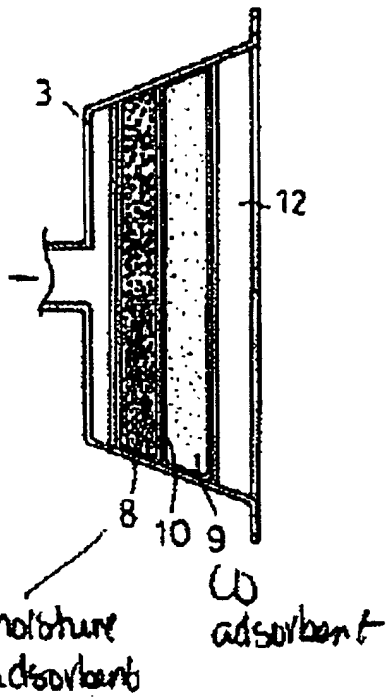


Fig. 3

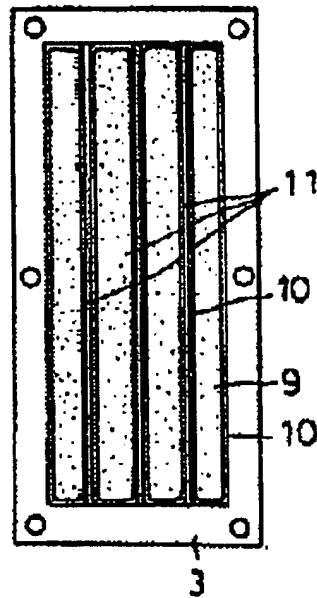
(a)



(b)



(c)



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